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ABSTRACT

The purpose of this paper is to provide process and cost elements for distillation of esterification water, which is an existing technique in the Division (Miranda and Sant-Celoni, plants in Spain).

UPR manufacturing leads to the production of esterification water on the basis of **6** to **10 %** of the amount of the thinned resin, depending on family (Ortho, iso, DCPD).

UPR esterification water deals with more than **92 %** of water, monomer losses from kettles (glycols, acids, and esters), and by-products. SPR and alkyds provides water with a lower concentration of glycols.

Incineration of water means between **100 to 200 €** per ton of effluent, so cheaper alternatives must be found.

Continuous distillation treatment is adapted to an effluent with quite constant composition, like in Miranda.

Batch distillation is more versatile and adapted to several kinds of waters. For example, Sant-Celoni batch columns deal with UPR and SPR waters, as well as alkyd water from Mollet plant.

Distillation of esterification water provides by-products (for incineration), water (further treatment or direct exit) and glycols mixture (re-use in UPR synthesis).

Since glycol can be recovered from esterification water, it is possible to heat faster, and to obtain shorter cycle time. However, the synthesis using recovered glycol with **20 %** of water is **½ h** longer in Miranda.

Energy consumption for such a duty is important (approximately **60 €** per ton of effluent). **Glycol savings** (**30 to 50 €** per ton of effluent) **hardly compensate energy and maintenance costs**.

Consequently, **distillation of esterification water is economically profitable only if :**

- Glycols from distillation can be easily re-used in synthesis.
- Water from distillation treatment can exit the plant without additional cost.
- Distillation avoids incineration or another expensive treatment in an external firm.

Thus, the savings relative to the non-incineration of water (**100** to **200 €** per ton of water) must be taken into account in the payback of a distillation treatment unit.

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INTRODUCTION

UPR manufacturing involves esterification water production on the following basis :

Resin family	Esterification water production (% of reactor RM)	Esterification water production (% of thinning tank FP)
Orthophtalic resin	9 - 10	6 – 7
Isophtalic resin	11 - 13	8 – 10
DCPD resin	10 - 12	7 - 9
PET resin	5	3

Table 1 : Esterification water production regarding resin family

Esterification water deals with the following composition (physical properties are supplied in appendix 1) :

Species	Content (weight %)	Origin
Water	92 - 93	Polyesterification, dehydration of glycols
Glycols / Acids / Esters	3 – 6	Reactants loss from reactor (mostly PG and MEG)
Propanal, acetaldehyde and acetone	< 1	Dehydration of PG through heating and acidic medium, leading preferentially to propanal.
p-dioxane and dioxolanes	< 1	Secondary reactions between glycols and their dehydration products
Allylic alcohol, acrolein	< 0.1	Equilibrium with propanal and acetone through heating and acidic medium.
Propionic and acetic acid, propylene and ethylene oxide	Traces	Oxidation products
Phenol, BTX		Impurity in raw materials
Toluene, Xylene		In case of solvent cooks
Hydrocarbons	Traces	DCPD cooks

Table 2 : Esterification water composition

Thus, UPR manufacturing results in tons of acidic aqueous effluent with COD of nearly **100 000 mg.L^{-1}**.

There are several alternatives to treat such an effluent.

This paper deals with distillation of esterification water as used by Sant-Celoni (batch distillation) and Miranda de Ebro (continuous distillation).

The interest is to remove a concentrated fraction of undesirable volatile compounds with high COD and incinerate it. Then, glycols can be recovered from water and re-used in low-color specification resins.

Eventually, water with low COD can be sent to a final treatment or directly to the sewer.

Nevertheless, energetic cost is important, and such a treatment required a good control of distillation parameters.

Elements for an economic evaluation based on data from Miranda and Sant-Celoni are supplied in this note.

1. Esterification water treatment

There is not an ideal technique for esterification water treatment. Advantages and drawbacks of each treatment must be analyzed to find out the best treatment for each plant. A non-exhaustive list of treatment is supplied in the following table :

Treatment	Advantage	Drawback	Experience
Incineration	● Full destruction of VOC in the absence of chlorinated products.	● Cost (nearly 200 €/MT).	CCP
Biological treatment	● Reduction of VOC (> 70 %). ● Aeration of effluent in an open tank achieves a reduction of VOC (possible in the absence of neighborhood). ● Average cost.	● Quite a lot of species are resistant to bio-oxidation. ● The bacteria are sensitive to pH, temperature, effluent concentration, and presence of phenol. ● An optimal aeration and nutrients feeding is required to achieve high yield of VOC reduction (> 90 %).	Drocourt Pasir Gudang Stallingborough Taboão
Decantation	● Elimination of upper organic with high COD by using gravity and/or demulsifier. ● Low cost.	● It is only a pre-treatment ● It only deals with effluents from solvent (BTX) cooks.	Isipingo Mumbai Pasir Gudang
Fenton	● Elimination of hardly oxidizable products through the actions of hydroxyl radicals.	● It requires a good control of reaction conditions.	Sant-Celoni Mumbai
Active carbon	● High efficiency. ● Recommendable for a final treatment (typically from 100 to 1 ppm).	● It doesn't hold concentrated flows ● High regeneration cost. ● Fire hazards in case of humidity.	Chonju
Distillation	● Removal of the organic fraction that is concentrated enough to decrease incineration cost. ● Recovery of glycols lost from reaction. ● Versatility	● The handling of such a distillation unit is not trivial. ● Energy consumption is high and must be optimized.	Miranda Sant-Celoni
Membrane	● Good efficiency.	● Membranes are not adapted to high flow rates, and are prone to fouling and blockage. ● This technology is not widespread, and not well known in the Division. ● Is this technique economically profitable?	None in UPR Brignoud (WBP)
Liquid-liquid extraction	● It works well when adequate solvent is found.	● Is there a solvent of undesirable products that could be decanted from water ?	None
Ozonolysis	● It does not require storage of ozone (generation in situ). ● High oxidizing power.	● Health and safety issues with ozone. ● Oxidization is not well controlled and by-products can even be worse than those before treatment.	Taboão (test)

Table 3 : Treatment used for aqueous effluent in UPR plants

2. Distillation unit for esterification water treatment

Esterification water may be considered as mixture of light compounds, water, and glycols and non-condensable products.

From Sant-Celoni experience, it is convenient to separate esterification water containing NPG from conventional esterification water. Otherwise, a dioxolane with strong smell is formed.

In both continuous and batch distillations, it is possible to re-process glycols or purified water.

2.1. Continuous distillation unit

A continuous distillation unit is suitable for plants with a single kind of effluent.

Esterification water production is not continuous, but a storage tank and a pump allow a continuous feed to the distillation unit boiler. A scheme of the distillation unit is supplied in figure 1.

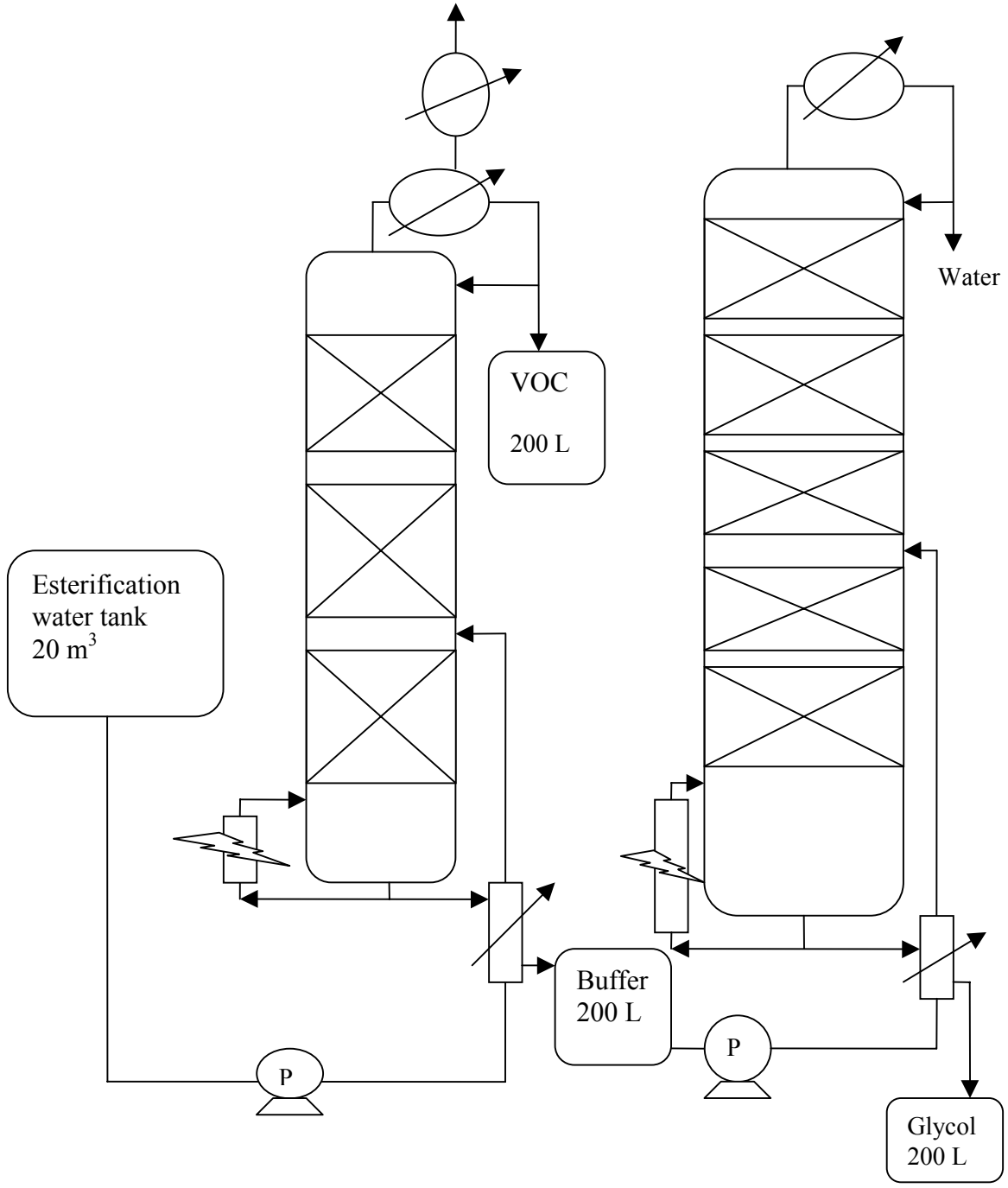

Figure 1: Simplified scheme of Miranda continuous distillation unit

The distillation unit deals with two columns :

- In the first one, light compounds are removed from esterification water, at the top of the column. This fraction roughly means **2 %** of the effluent. It must be incinerated, unless it can be sold to another company. The bottom product of the first column is sent to the second one.

- In the second one, glycols and esters are recovered at the bottom, though purified water exits through the condenser of the column.

The first column should have at least **5** theoretical plates, runs at atmospheric pressure with a consistent reflux (higher than **2.0**) at the top of the column to avoid water entrainment, and high incineration cost.

N.B: *Reflux means the ratio between the condensed liquid that returns to the top of the column and the condensed liquid that goes to the distillate receiver.*

Temperature at the top of first column must be higher than **80 °C** to make sure that dioxolanes goes to the distillate. Vapor flow must be under-condensed at **25 °C** to avoid smell troubles due to ketones and aldehydes.

The second column runs with **3** to **5** theoretical plates, preferably under vacuum, with a reflux from **1.0** to **2.0** at the top of the column.

In these conditions, a mixture with **70 - 80 %** of glycols is recovered at the bottom. Water with COD of about **4 000 mg.L^{-1} (ppm)** exits the condenser. As a rule, authorized limit of COD at plants outlet is between **200** and **500 mg.L^{-1}**, which means that a final treatment is necessary.

Filters must be situated at the inlet of the two columns to prevent blockage caused by phtalic acid, isophtalic acid, maleic acid, NPG and others.

To optimize energy consumption, it is recommendable to use heat exchanger to contact cold liquid at the inlet of a column with hot liquid exiting the bottom (or boiler).

2.2. Batch distillation unit

A batch distillation unit is more adapted to plants with different kind of resin, for example UPR, SPR and alkyds at the same time (configuration of Chonju, Mumbai, Pasir Gudang, Stallingborough, Sant-Celoni).

In this case, a single column is convenient: boiler is loaded with esterification from storage tank, and then fractionated distillation takes place.

Obviously, depending on the volume of esterification water, several columns in parallel may be used.

The column must run with more than **5** theoretical plates at the beginning, and should preferably be run under vacuum at the end of the batch.

3. Data from CRAY VALLEY IBERICA

The data were supplied by J.I. ROYO (Miranda), M. MORALES and C. TRUJILLO (Sant-Celoni).

3.1. Glycol issue

The following table provides the volumes of crude esterification water that were distillated, as well as glycols recovered :

Glycol recovery		Miranda	Sant-Celoni
Distillation	Kind	Continuous	Batch
Origin of effluent	Production unit	UPR	UPR SPR Alkyds (Mollet)
Crude esterification water	MT / year	1 083	4 760
Unit treatment capacity	kg crude effluent / h	200	670 (batch h)
Glycols mixture recovered	MT / year	132	280
Glycol content in glycol mixture	weight % of glycol mixture	70 - 80	70 – 80
Equivalent of pure glycol recovered (*)	MT / year	79	196
Glycol recovery	Weight % of crude effluent	7.3	4.1 (**)

Table 4 : Glycol recovery data in Miranda and Sant-Celoni plants

(*) : It refers to the amount of pure PG that can be saved in a further resin synthesis.

(**) : Effluent of Sant-Celoni is less concentrated in glycols than effluent of Miranda.

3.2. Practices regarding re-use of recovered glycol

Glycol recovery from esterification water is economically profitable if this glycol may be used in some recipes with low specification regarding Hazen color.

Such a recipe may be mass resin for thixotropic resin containing cobalt.

The NORSODYNE 1312L recipe from Miranda is supplied in table 5a and 5b :

Raw material	Amount (kg)	Amount (mole) (base: all acid is 1.0 mole)
Maleic anhydride	1 788	0.502
Phtalic anhydride	2 685	0.498
Propylene glycol	2 945	1.06

Table 5a : NORSODYNE 1312L with pure PG only

Raw material	Amount (kg)	Amount (mole) (base: all acid is 1.0 mole)
Maleic anhydride	1 788	0.502
Phtalic anhydride	2 685	0.498
Pure PG (from bulk storage)	2 625	0.95
PG from distillation	550	0.11

Table 5b : NORSODYNE 1312L by using PG from distillation

From these figures:

- **17 %** of PG necessary in the recipe is substituted from PG recovered in the distillation unit.
- **550 kg** of recovered PG equals **320 kg** of pure PG (**58 %**).

3.3. Cost issue

Cost data are supplied in table 6 :

Cost data	Units	Miranda plant	Sant-Celoni plant
Date of project		1 992	1 994
Investment cost	k€	150	120
Vapor consumption	Ton vapor / MT crude effluent	Not available	2.38 (*)
Glycol recovery	MT glycol recovered / MT crude effluent	0.073	0.041
Glycol saving	€ / MT crude effluent (basis of 702 € / MT PG)	51	29

Table 6 : Cost data from Miranda and Sant-Celoni

In the case of a distillation unit, only **2 %** of crude effluent have to be incinerated, which corresponds to the light compounds fraction.

Incineration cost is nearly **200 € / MT**, which means **4 € / MT** esterification water, when a distillation unit is used.

Due to the important energy consumption, savings due to glycol recovery are not enough to make this treatment economically profitable.

In fact, in the assumption that vapor cost is **26 €** per ton of vapor, then energy cost is nearly **60 € / MT** esterification water.

Nevertheless, **several favorable scenarios exist**:

- A plant with an excess of energy (e.g.: Drocourt plant with its maleic anhydride facility)
- A plant where distillation of esterification water avoids the incineration issue, or another expensive treatment in an external firm.

Conclusion

Distillation of esterification water allows obtaining separate streams of organic by-products (sent to incineration), water (sent to a further treatment or to the sewer if its content is compliant with local environmental requirements), and glycols (re-used in UPR synthesis).

Continuous distillation treatment is adapted to plants that produce a single kind of effluent, e.g. Miranda with UPR esterification water.

Batch distillation is more suitable for plants with different effluent, e.g. Sant-Celoni with both UPR and SPR waters, as well as alkyd water from Mollet plant.

Investment for Miranda and Sant-Celoni esterification water distillation unit was respectively **150 k€** in 1992, and **120 k€** in 1994.

Less glycols per ton of effluent are recovered in Sant-Celoni because UPR water is blended with SPR and alkyd resin water.

Energy consumption for such a duty is important (approximately **60 €** per ton of effluent). **Glycol savings** (**30 to 50 €** per ton of effluent) **hardly compensate energy and maintenance costs**.

Consequently, **distillation of esterification water is economically profitable only if :**

- Glycols from distillation can be easily re-used in synthesis.
- Water from distillation treatment can exit the plant without additional cost.
- Distillation avoids incineration or another expensive treatment in an external firm.

Appendix 1 : Boiling points of esterification water components

Depending on the raw materials, many species may be found in the esterification water. They are presented below by growing boiling points. Components indicated in gray are a common occurrence in CRAY VALLEY.

Component	Formula	n° CAS	Specific gravity at 25°C ($kg.m^{-3}$)	Molecular weight ($g.mol^{-1}$)	Boiling point at 1 atm (°C)	Melting point at 1 atm (°C)
Ethylene oxide	C_2H_5O	75-21-8	866	44	13	-111
Acetaldehyde	C_2H_4O	75-7-0	774	44	21	-121
Propanal	C_3H_6O	123-38-6	790	58	48	-103
Propylene oxide	C_3H_6O	75-56-9	822	58	34	-112
Acrolein	C_3H_4O	107-2-8	833	56	53	-88
Acetone	C_3H_6O	67-41-1	785	58	56	-95
Allylic alcohol	C_3H_6O	107-18-6	846	58	97	-129
Dioxolanes	A few data are available in the literature, except for 1,3-dixolane. Boiling point for derivatives of 1,3-dixolane is 80-90 °C (experience from Miranda).					
1,3-dixolane	$C_3H_6O_2$		1 060	58	78	-95
2EDD	$C_7H_{14}O_2$	2-ethyl-5,5-dimethyl-1,3-dioxolane				
DMD	$C_5H_{10}O_2$	2,4-dimethyl-1,3-dioxolane	941	102	92.5	
EMD	$C_6H_{12}O_2$	2-ethyl-4-methyl-1,3-dioxolane	935	116	118	
Water	H_2O	7732-18-5	994	18	100.0	0.0
1,4-dioxane	$C_4H_8O_2$	123-91-1	1 027	88	101	12
Toluene	C_7H_8	108-88-3	863	92	111	-95
Acetic acid	$C_2H_4O_2$	64-19-7	1041	60	118	17
Propionic acid	$C_3H_6O_2$	79-9-4	987	74	141	-21
Xylene	$C_8H_{10}O$	95-47-6	875	106	144	-25
Phenol (*)	C_6H_6O	108-95-2	1 070	94	182	41
PG	$C_3H_8O_2$	57-55-6	1 032	76	188	-60
MEG	$C_2H_6O_2$	107-21-1	1 109	62	197	-13
NPG	$C_5H_{12}O_2$	126-30-7	891	104	206	130
DEG	$C_4H_{10}O_3$	111-46-6	1 113	106	245	-11

(*) : Depending on suppliers, traces of phenol (or BTX) may be found in some raw materials , and then in the effluent.

When esterification water is free of BTX, the mixture tends to form a single phase. Dioxolanes are miscible with water, but this miscibility decreases with the substitution of the ether cycle.

In Miranda plant, the mixture between the most volatile compounds (propanal, acetone, dioxolanes) happens to form two phases in the distillate of the first distillation column.